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TITLE: PHENOLIC COCONDENSATION RESIN AND ITS PRODUCTION

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ABSTRACT:

PURPOSE: To obtain the subject resin comprising the sulfomethylation product of a specific phenolic cocondensate, having good water solubility, long in the pot life, capable of being cured at the ordinary temperature, and giving cured products excellent in water resistance, oil resistance and weather resistance, and useful for adhesives, binders, etc.

CONSTITUTION: The objective resin comprises the sulfomethylation product of the early cocondensate of (A) a monohydric phenol.aldehyde condensate having methylol groups with (B) a polyhydric phenol or polyhydric phenol.aldehyde early condensate. The resin is preferably furthermore mixed with an aldehyde-donating agent such as an aldehyde or trioxane or an alkylolated triazone derivative as a curing agent. The sulfonation product in the objective resin is obtained by reacting the condensate of the component A, the condensate of component B or the cocondensate of the components A and B with a sulfomethylating agent such a water-soluble sulfite salt or a hydroxymethane

1. sulfonate salt before, during or after the production of the condensate or cocondensate.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention relates to the manufacture technique of the phenol system copolycondensation resin used for adhesives, such as wood, paper, rubber, synthetic resin, inorganic and organic fiber, and a metal, a binder, an impregnant, a coating agent and a coating vehicle, a laminate, a grinding stone, a shell mold, a brake, and rubber combination.

[0002]

[Background of the Invention] The resol type phenol resin to which a methanol, ethanol, etc. are made into a solvent from the former, and the room temperature setting of the acid catalyst is added and carried out as a phenol system resin hardened in ordinary temperature at the time of use, and the 1 \*\* phenol-polyhydric-phenol copolycondensation resin to which the copolycondensation of the 1 \*\* phenol is carried out to an aldehyde with polyhydric phenols, such as a resorcinol and an alkyl resorcinol, and the room temperature setting of the aldehyde is added and carried out as a curing agent at the time of use are offered.

[0003] A pyrogenetic reaction is carried out under alkaline catalyst presence, and the above-mentioned resol type phenol resin obtained as alkaline aqueous solution does not harden them in ordinary temperature, although 1 \*\* phenol and an aldehyde are hardened by heating. In order to stiffen this in ordinary temperature, it is required to add an acid catalyst and to make it harden by the acidity side, as described above. However, pH of water solubility was [ below neutrality ] bad, and in order to improve the solubility of the initial condensate by the side of acidity, when the room temperature setting of this first time condensate was carried out and it had to be used as the solution of organic solvents, such as alcohol and a ketone, it had a \*\*\*\* fault. On the other hand, in the case of the above-mentioned 1 \*\* phenol-polyhydric-phenol copolycondensation resin, addition of an aldehyde curing agent knows carrying out a room temperature setting in all the fields of pH. However, when hardening is quick, a working life is short and handling was inconvenient, there was a \*\*\*\* fault in this copolycondensation resin. Since a cure rate is still quick than the case where it is a resorcinol when especially a polyhydric phenol is an alkyl resorcinol like 5 \*\*\*\*\* resorcinol, the above-mentioned fault will become still serious.

[0004]

[Description of the Prior Art] The condensate which improves the solubility of this condensate and maintains water solubility also in the domain of pH of 1-10.5 under presence of hydrophilic organic solvents, such as some alcohol, is offered by resol type phenol resin's carrying out the addition reaction of the water-soluble inorganic sulfite, and introducing a sulfo methyl group into it as a means for improving the water solubility of the above-mentioned resol type phenol resin, (U.S. patent of No. 2,537,798). Moreover, as technique of adjusting the cure rate of the above-mentioned 1 \*\* phenol-polyhydric-phenol copolycondensation resin, the technique of adding complexing agents, such as an acetone and a caprolactam, is offered (Provisional Publication No. 47-34892).

[0005]

[Problem(s) to be Solved by the Invention] However, by the technique of carrying out sulfo methylation, in order to improve the water solubility of the above-mentioned resol type phenol resin, if phenol resin carries out a room temperature setting and a room temperature setting is not carried out to the bottom of presence of an acid catalyst neutrality or under alkaline, there is a \*\*\*\* fault. Moreover, the fault to which water solubility becomes bad by the acidity side is not improved, but when it is an alkyl resorcinol, especially this inclination is remarkable [ the technique of the retardation effect of the setting time of adjusting the cure rate of the above-mentioned 1 \*\* phenol-polyhydric-phenol copolycondensation resin by the above-mentioned complexing agent is in addition inadequate, and / as for this copolycondensation resin ]. Therefore, it did not alkaline-come to accept it, but also neither in neutrality nor an acid field, water solubility was maintained as much as possible, it was concerned with the acid and alkaline situation, but the room temperature setting was carried out in the large field, and the thing for which the resin with a moderate cure rate and a moderate working life is found out was the very important technical problem of a phenol system copolycondensation resin.

[0006]

[Means for Solving the Problem] When this invention person made the sulfo methyl group exist in the copolycondensation object with 1 \*\* phenolaldehyde condensate, the polyhydric phenol and/or the polyhydric phenol, and the initial condensate of an aldehyde which has a methylol machine, it found out that an acidity side was also effective in carrying out a room

temperature setting in all pH fields if an aldehyde and/or an aldehyde donator are added as a curing agent at the same time water solubility increases, and the cure rate of a copolycondensation object being delayed moreover, and a working life being extended. namely, this invention as a means for solving the aforementioned conventional technical problem It is what offers the phenol system copolycondensation resin which is the sulfo methylation object of the initial copolycondensation object (C) with 1 \*\* phenolaldehyde condensate (A), the polyhydric phenol and/or the polyhydric phenol, and the initial condensate of an aldehyde (B) which has a methylol machine. The above-mentioned phenol system copolycondensation resin carries out the condensation reaction of 1 \*\* phenol, an aldehyde, and/or the aldehyde donator under alkaline, and generates the initial condensate (A) of 1 \*\* phenolaldehyde. Subsequently, it gets poisoned by manufacturing the initial copolycondensation object of an aldehyde of 1 \*\* phenol and a polyhydric phenol (C) by adding and carrying out the copolycondensation of a polyhydric phenol and/or a polyhydric phenol, and the initial condensate (B) of an aldehyde to this first time condensate. It is manufactured by the technique of carrying out the addition reaction of the sulfo methylation agent, after a reaction before this condensation reaction or this copolycondensation reaction or in a reaction.

[0007] this invention is explained in detail below.

With 1 \*\* phenol in [\*\* 1 Phenol] this invention Alkylphenols, such as a phenol, o-cresol, m-cresol, p-cresol, ethylphenol, iso-propyl phenol, a xylenol, 3, 5-xylenol, butylphenol, t-butylphenol, and a nonyl phenol, o-fluorophenol, m-fluorophenol, p-fluorophenol, o-chlorophenol, m-chlorophenol, p-chlorophenol, o-\*\*\*\*\* phenol, m-\*\*\*\*\* phenol, p-\*\*\*\*\* phenol, o-iodine phenol, m-iodine phenol, p-iodine phenol, ortho aminophenol, m-aminophenol, para aminophenol, ortho nitrophenol, m-nitrophenol, p-nitrophenol, a 2, 4-dinitrophenol, 2, 4, A kind of 1 \*\* phenols, such as 1 \*\* phenol substitution products, such as 6-trinitrophenol, and a naphthol, or two sorts or more of mixture is said.

[0008] Although the polyhydric phenols of a [polyhydric-phenol] this invention are a kind of polyhydric phenols, such as a resorcinol, an alkyl resorcinol, pyrogallol, a catechol, an alkyl catechol, hydroquinone, alkyl hydroquinone, a phloroglucine, a bisphenol, and dihydroxy naphthalene, or two sorts or more of mixture, a desirable thing is a resorcinol or an alkyl resorcinol among these polyhydric phenols, and especially a desirable thing is an alkyl resorcinol with the reaction rate quicker than a resorcinol with an aldehyde. As the above-mentioned alkyl resorcinol For example, 5-methyl resorcinol, 5-ethyl resorcinol, 5-propyl resorcinol, a 5-n-butyl resorcinol, 4, 5-dimethyl resorcinol, 2, 5-dimethyl resorcinol, 4, 5-diethyl resorcinol, 2, 5-diethyl resorcinol, 4, 5-dipropyl resorcinol, There are 2, 5-dipropyl resorcinol, a 4-methyl-5-ethyl resorcinol, a 2-methyl-5-ethyl resorcinol, a 2-methyl-5-propyl resorcinol, 2 and 4, a 5-trimethyl resorcinol, 2 and 4, a 5-triethyl resorcinol, etc. Since the polyhydric-phenol mixture obtained by dry distillation of the Estonia \*\* oil shale contains various reactant high alkyl resorcinols besides 5 \*\*\*\*\* resorcinol so much cheaply, it is the most desirable polyhydric-phenol raw material to this invention.

[0009] With the aldehyde and/or aldehyde donator in a [aldehyde donator] this invention An aldehyde and the compound which will carry out generation supply of the aldehyde if it decomposes are meant. Formalin, formaldehyde, a paraformaldehyde, a trioxane, an acetaldehyde, a propionaldehyde, a polyoxymethylene, a trichloroacetic aldehyde, a hexamethylenetetramine, a furfural, glyoxal, n-butyraldehyde, a caproaldehyde, Kinds, such as an allyl-compound aldehyde, the Benz aldehyde, a crotonaldehyde, an acrolein, a tetrapod oxy-methylene, a phenylacetaldehyde, o-torr aldehyde, and a salicylaldehyde, or two sorts or more of mixture is illustrated.

[0010] As a sulfo methylation agent used in a [sulfo methylation agent] this invention, hydroxy alkane sulfonic acids, such as a water-soluble sulfite with quaternary amines, such as a sulfurous acid, a pile sulfurous acid or a meta-pile sulfurous acid, alkali metal or a trimethylamine, and benzyl trimethylammonium, or the fourth class ammonium and hydroxy methanesulfon acid chloride obtained by the reaction of these water-soluble sulfites and aldehydes, are illustrated. This water-soluble sulfite reacts with the methylol machine of the initial copolycondensation object (C) with the initial condensate (A) of 1 \*\* phenolaldehyde, a polyhydric phenol and/or a polyhydric phenol, and the initial condensate (B) of an aldehyde, forms a hydroxy alkane sulfonate with an aldehyde first in response to the time of generating a sulfo methyl group or making the above-mentioned condensate (A) and/or an initial condensate (B) condense, subsequently reacts with a phenol, and generates a sulfoalkyl machine. Therefore, hydroxy alkane sulfonates, such as hydroxy methanesulfon acid chloride, can also be used as a sulfo methylation agent instead of a water-soluble sulfite.

[0011] In a [third-component] this invention in addition to 1 \*\* phenol, a polyhydric phenol, an aldehyde donator, a sulfo methylation agent, a condensation catalyst, and a complexing agent as a third component a request -- if -- a urea, a melamine, thiourea, benzoguanamine, toluene, a xylene, a cumarone, a cyclohexanone, cashew oil, tannin, \*\*\*\*\*, a shellac, rosin or a rosin derivative, a petroleum resin, a methanol, ethanol, and an isopropanol -- Kinds, such as n-butanol, an isobutanol, ethylene glycol, a diethylene glycol, a polyethylene glycol, a glycerol, furfuryl alcohol, the linseed oil, tung oil, and castor oil, or two sorts or more are made into a copolycondensation agent or a modifier. At the time of reaction start of condensation or a copolycondensation Among a reaction or after a reaction end, it adds, and even if it denaturalizes, it does not interfere.

[0012] The phenol system copolycondensation resin of a [manufacture of phenol system copolycondensation resin] this invention is manufactured by the condensation reaction and sulfo methylation reaction of two phases which are called generation of the initial copolycondensation object (C) by the copolycondensation reaction with generation of the initial condensate (A) of 1 \*\* phenolaldehyde by the condensation reaction with 1 \*\* phenol, an aldehyde, and/or an aldehyde donator and this first time condensate (A) and a polyhydric phenol, and/or a polyhydric phenol and the initial condensate of an aldehyde (B). In the first condensation phase, if required for one mol of 1 \*\* phenols, an aldehyde, and/or 1-4 mols of aldehyde donators, a solvent and a third component will be added, an alkali compound is added, pH is prepared to 8-11, a

pyrogenetic reaction is carried out at 55-100 degrees C of solution temperature for 8 to 20 hours, and the initial condensate (A) of 1 \*\* phenolaldehyde which has a methylol machine is obtained. At this time, the whole quantity, in addition \*\* of an aldehyde and/or an aldehyde donator are good at the time of reaction start, and they may carry out split addition or continuity instillation. As an alkali compound used for the above-mentioned condensation system of reaction, for example, alkali metal, Salts, aminess, etc., such as hydroxides, such as alkaline earth metal, an oxide, a carbonate, acetate, and phosphate, are used. For example, a sodium hydroxide, a potassium hydroxide, a barium hydroxide, a calcium hydroxide, a sodium carbonate, lime, a sodium sulfite, potassium sulfite, a sulfurous-acid lithium, sodium acetate, sodium phosphate, ammonia, a trimethylamine, a triethylamine, Alkali compounds, such as a monoethanolamine, a diethanolamine, a triethanolamine, a hexamethylenetetramine, and a pyridine, are used. When a sulfurous-acid alkali-metal salt is used, it acts also as a sulfo methylation agent only as an alkali compound. The addition of the above-mentioned alkali compound is usually added in 6% or less of an amount severalpercent or less to the weight of 1 \*\* phenol. In the 2nd phase of condensation, a polyhydric phenol and/or a polyhydric phenol, and the initial condensate (B) of an aldehyde are added to the initial condensate (A) of the 1st phase, if still required, an aldehyde and/or an aldehyde donator, a solvent, and a third component will be added, a pyrogenetic reaction is carried out at 60-110 degrees C of solution temperature for 1- 10 hours, and an initial copolycondensation object (C) is obtained. In order for the total amount of the polyhydric phenol added here to be usually 0.01-3 mols and also to carry out [ as opposed to / one mol of 1 \*\* phenols / in order to improve the solubility of an initial copolycondensation resin (C) and to aim at retardation of a cure rate ] the room temperature setting of this first time copolycondensation resin (C) using a curing agent, it is usually 0.3 mols or more desirably 0.2 mols or more. The above-mentioned copolycondensation reaction is performed under alkaline like the case where an initial condensate (A) is generated, or is performed neutrality or under acid. In order to be able to use the same alkali compound as what was used when condensing an initial condensate (A), in order to have adjusted this copolycondensation reaction alkaline and to adjust neutrality or acid For example, a hydrochloric acid, a boric acid, oxalic acid, formic acid, an acetic acid, a lactic acid, a butyric acid, Para toluenesulfonic acid, A phenolsulfonic acid, a benzenesulfonic acid, a naphthalene-alpha-sulfonic acid, The ester of organic acids, such as inorganic [ , such as a naphthalene-beta-sulfonic acid ], an organic acid, or oxalic acid dimethyl ester Acid anhydrides, such as a maleic-acid anhydride and a phthalic-acid anhydride, an ammonium chloride, An ammonium sulfate, an ammonium nitrate, an ammonium oxalate, an ammonium acetate, Ammonium salts, such as ammonium phosphate, an ammonium thiocyanate, and imido sulfonic-acid ammonium Organic halogenides, such as monochloroacetic acid and its specific-salt, alpha, and alpha' dichlorohydrin, Acid compounds, such as urea adducts, such as a hydrochloride of aminess, such as a triethanolamine hydrochloride and an aniline hydrochloride, a salicylic-acid urea adduct, a stearin acid urea adduct, and an oenanthic-acid urea adduct, an N-trimethyl taurine, a zinc chloride, and ferric chloride, are used. moreover, the polyhydric phenol and the initial condensate of an aldehyde (B) used for a copolycondensation reaction -- the polyhydric phenol of one mol -- receiving -- 0.1-0.7 mols of aldehyde donators -- if required [ come out comparatively and ] in addition -- a solvent, a complexing agent, and a third component -- adding -- pH 1-12 -- it is the initial condensate which carries out a pyrogenetic reaction for 1- 10 hours, and is preferably obtained at 60-110 degrees C of pH three to 11 solution temperature In this invention, you may add the complexing agent which mitigates the reactivity of a polyhydric phenol and an aldehyde in the case of the copolycondensation reaction of a copolycondensation object (C) in the case of the condensation reaction of an initial condensate (B). The compound which has a ketone group or an amide group etc. which has complexing organization potency to the hydroxyl of a polyhydric phenol as such a complexing agent is raised, for example, an acetone, a caprolactam, etc. are illustrated, and especially an acetone is a desirable complexing agent. Although especially a limit does not have the addition of a complexing agent, about 0.4-0.8 mols of complexing agents are usually desirable to the polyhydric phenol of one mol. Although the indifferent water is used as a solvent in this invention If required, further A methanol, ethanol, an isopropanol, n-propanol, an isopropanol, n-butanol, an isobutanol, sec-butanol, t-butanol, n-amyl alcohol, isoamyl alcohol, n-hexanol, A methyl amyl alcohol, 2-\*\*\*\*\* Norian, n-heptanol, n-octanol, trimethyl nonyl alcohol, a cyclohexanol, benzyl alcohol, furfuryl alcohol, a tetrahydrofurfuryl alcohol, loon ethyl alcohol, Alcohols, such as diacetone alcohol, an acetone, a methyl acetone, a methyl ethyl ketone, a methyl-n-propyl ketone, a methyl-n-butyl ketone, a methyl isobutyl ketone, a diethyl ketone, a G n-propyl Ketones, such as a ketone, a diisobutyl ketone, an acetonylacetone, a methyl oxide, a cyclohexanone, a methylcyclohexanone, an acetophenone, and camphor Glycols, such as ethylene glycol, a diethylene glycol, a triethylene glycol, a propylene glycol, a trimethylene glycol, and a polyethylene glycol Glycol ethers, such as an ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, an ethylene glycol isopropyl ether, the diethylene-glycol monomethyl ether, and the triethylene-glycol monomethyl ether The ester, the derivatives of those of the above-mentioned glycols, such as an ethylene glycol diacetate and diethylene-glycol-monoethyl-ether acetate, The addition use of independent or two or more sorts of mixture of water fusibility organic solvents, such as ether, such as 1 and 4-dioxane, a diethyl cellosolve, a diethyl carbitol, ethyllactate, isopropyl lactate, a diethylene glycol diacetate, and a dimethylformamide, can be carried out. While an acetone etc. is a solvent, it acts also as a complexing agent of an alkyl resorcinol, and brings a quieter reaction. Sulfo methylation is performed [ in / condensation with 1 \*\* phenol of the 1st phase, an aldehyde, and/or an aldehyde donator ] in condensation with a polyhydric phenol, an aldehyde, and/or an aldehyde donator in the copolycondensation with the initial condensate of 1 \*\* phenolaldehyde of the 2nd phase (A), a polyhydric phenol and/or a polyhydric phenol, and an aldehyde condensate (B) by adding and carrying out the pyrogenetic reaction of the above-mentioned sulfo methylation agent before a reaction or in a reaction, and after a reaction. However, since sulfo methylation in the condensation phase with a polyhydric phenol, an aldehyde, and/or an aldehyde donator has [ especially in

the case of the polyhydric-phenol condensate without a methylol machine ] a possibility of reducing the functionality with little polyhydric phenol further in the case of an alkyl resorcinol, it is not desirable technique. the addition of a sulfo methylation agent -- usually -- one mol of 1 \*\* phenols -- receiving -- a sulfo methylation agent -- although it is 0.001-1.5 mols, in order to hold performances, such as the hardenability of the initial copolycondensation object after condensation, and the physical properties of the resin after hardening, good, it is desirable that the addition of a sulfo methylation agent is about 0.01-0.8 mols Thus, the part and sulfo methylation agent of a methylol machine of 1 \*\* phenol, a polyhydric phenol, and the initial copolycondensation object (C) of an aldehyde react, or when a sulfo methylation agent is a hydroxy alkane sulfonate, it reacts with a part of phenol of this copolycondensation object (C), and a sulfo methyl group is formed, and the phenol system copolycondensation resin of this invention is manufactured.

[0013]

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